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KINETICS AND MECHANISM OF CATALYTIC HYDROPROCESSING
OF COMPONENTS OF COAL-DERIVED LIQUIDS

Twentieth Quarterly Report for the Period
February 16—May 15, 1984

By
Bruce C. Gates
Jon H. Olson
G. C. A. Schuit
Alvin B. Stiles
Leon Petrakis

June 26, 1984
Date Published

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University of Delaware
Newark, Delaware

and

Gulf Research and Development Company
Pittsburgh, Pennsylvania

MASTER

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February 16, 1984 to May 15, 1984

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ABSTRACT

Kinetics data have been determined for the catalytic hydroprocessing of the acidic fractions of a heavy distillate of a liquid derived from Powhatan No. 5 coal. A commercial, sulfided Ni-Mo/ γ -Al₂O₃ catalyst was used in the experiments, carried out at 350°C and 120 atm with the coal liquid fractions dissolved in cyclohexane. The feed and hydrotreated products were analyzed by gas chromatography/mass spectrometry. The data were analyzed with group-type methods for compound classes, and results were also obtained for some individual organooxygen compounds. Catalytic hydroprocessing leads to a large increase in the number of compounds and a shift to lower boiling ranges. The data are broadly consistent with reaction networks determined with pure compounds; the most important reactions include aromatic ring hydrogenation, hydrodeoxygenation, and hydrodemethylation. Pseudo first-order rate constants for conversion of the predominant organooxygen compounds are on the order of 10⁻⁴ L/(g of catalyst·s); the reactivity decreases in the order cyclohexylphenol > dimethylhydroxyindane > tetrahydronaphthol > phenylphenol > 1-naphthol.

II. OBJECTIVES

Statement of Work Outline

- A. Preparation of coal liquid fractions and pure compounds for hydroprocessing reaction studies
 1. Fractions of coal-derived liquids separated by preparative chromatography
 2. Detailed characterization of each fraction
- B. Conversion of coal-liquid fractions in high-pressure microreactors
 1. Ni-Mo/ Al_2O_3
 2. Co-Mo/ Al_2O_3
 - *3. Aged H-Coal catalysts
- C. Analysis of reaction products
 1. Physical and chemical characterization
 2. Determination of relative reactivities for hydrogenation, hydrocracking, and removal of heteroatoms
 - **3. Formulation of reaction networks
- D. Investigation of the role of hydrogen-donor molecules in catalytic hydrogenation and hydrodenitrogenation of synthetic coal-derived liquid fractions
 1. Hydrogen-transfer reactants--biphenyl, quinoline, and acridine separately in hexadecane carrier oil
 2. Three or more coreactants and inhibitors--quinoline, acridine, and carbazole in heterocyclic and aromatic solvents
 3. Synthetic coal-derived liquids with all important components proportionately represented
- E. Characterization of aged H-Coal catalyst by electron microscopy, microprobe analysis, and other physical methods
- F. Representation of results in terms of engineering reaction networks and kinetics.

*Insofar as time allows and samples can be obtained.

**As data warrant.

111. PROGRESS TO DATE: Work Schedule

IV. CUMULATIVE EXPENDITURES BY QUARTER

QUARTER	PERSONNEL	TRAVEL	SUPPLIES & EXPENSES	GULF SUBCONTRACT	EQUIPMENT	MISCELLANEOUS*	OVERHEAD
First 5/15/79- 8/15/79	14,101	\$—	178	\$—	\$—	\$—	5,718
Second 8/15/79- 11/15/79	31,539	325	2,779	16,632	—	100	14,754
Third 11/15/79- 2/15/80	40,952	893	5,077	32,754	10	1,726	20,495
Fourth 2/15/80- 5/15/80	50,521	2,481	8,071	55,571	10	1,726	26,101
Fifth 5/15/80- 8/15/80	66,383	2,485	10,788	66,162	2,510	1,726	32,513
Sixth 8/15/80- 11/15/80	89,428	4,612	15,968	71,095	3,232	2,437	44,938
Seventh 11/15/80- 2/15/81	110,060	4,823	17,378	77,966	3,233	2,437	53,839
Eighth 2/15/81- 5/15/81	131,318	4,823	24,672	82,777	9,419	2,437	65,260
Ninth 5/15/81- 8/15/81	159,870	4,829	29,687	88,658	24,479	2,965	78,900
Tenth 8/15/81- 11/15/81	176,469	6,744	31,486	92,679	24,479	2,965	87,025
Eleventh 11/15/81- 2/15/82	185,110	7,378	35,437	108,616	23,519	4,140	92,786
Twelfth 2/15/82- 5/15/82	192,289	9,368	41,799	119,695	26,121	4,920	99,173
Thirteenth 5/15/82- 8/15/82	200,575	10,480	48,510	125,900	26,121	6,815	106,512
Fourteenth 8/15/82- 11/15/82	210,071	10,837	49,947	131,900	26,121	6,815	109,632

IV. CUMULATIVE EXPENDITURES BY QUARTER

Fifteenth 11/15/82- 2/15/83	227,770	12,022	54,234	132,000	26,121	7,237	115,836
Sixteenth 2/15/83- 5/15/83	226,911	12,179	58,855	132,000	26,121	7,848	119,493
Seventeenth 5/15/83- 8/15/83	234,434	12,179	69,187	132,000	26,121	7,748	126,635
Eighteenth 8/15/83- 11/15/83	242,309	12,179	71,063	132,000	26,121	8,387	130,011
Nineteenth 11/15/83- 2/15/84	245,890	12,179	71,707	132,000	26,121	8,553	131,768
Twentieth 2/15/84- 5/15/84	249,940	12,179	72,098	132,000	26,121	8,553	132,764
BUDGET	\$217,102	\$15,000	\$88,000	\$132,000	\$30,000	\$42,808	\$143,128

*Maintenance, Info. Processing

TOTAL BUDGET: \$660,945 TOTAL EXPENDED TO DATE: \$633,655

INTRODUCTION

Hydrodeoxygenation is a class of catalytic hydroprocessing reaction that has received scant attention because the oxygen content of petroleum is almost negligibly low. But the need for alternative energy sources has focused attention on coal and shale, which have much higher oxygen contents. The liquid fuels derived from these sources contain compounds typified by 1-naphthol and dibenzofuran (Grandy *et al.*, 1984); reaction networks for catalytic hydrogenation/hydrodeoxygenation of a few of these compounds have been recently reported (Krishnamurthy *et al.*, 1981; Li *et al.*, 1984A; Furimsky, 1983).

Our approach to the determination of the reactivities of organooxygen compounds in synthetic fuels has involved (1) liquid-chromatographic fractionation of a heavy distillate derived from hydroliquefied Powhatan No. 5 coal into classes of compounds distinguished by chemical types (Petrakis *et al.*, 1983A) and (2) investigation of the reactions of the individual fractions with hydrogen under carefully controlled conditions in a high-pressure catalytic microreactor. The acidic fractions of the coal liquid contain high concentrations of substituted naphthols and related compounds (Petrakis *et al.*, 1983B; Grandy *et al.*, 1984). The first experiments characterizing the reactivities of the weak- and very-weak-acid fractions have been

reported (Li et al., 1984B). Characterization of the reactants and products by combined gas chromatography/mass spectrometry (GC/MS) determined quantitative reactivities of the several major organooxygen compounds in the presence of sulfided Ni-Mo/ γ -Al₂O₃ catalyst under hydroprocessing conditions representative of potential industrial applications.

In the work described here, we have taken the feed and product samples obtained in the above-mentioned work and characterized them exhaustively by GC/MS. The additional data have been analyzed by group-type methods, the results determining activities of several classes of compounds; further, improved GC/MS capability has provided reactivity information for individual compounds which was not attainable in the earlier experiments.

EXPERIMENTAL SECTION

Materials

The catalyst, a standard, commercial NiO-MoO₃/ γ -Al₂O₃ (Houalla et al., 1978), and the coal-liquid fractions (Petrakis et al., 1983A,B) have been described in detail. The two coal-liquid fractions (the weak acids and the very weak acids) were dissolved in cyclohexane and used as feeds to an isothermal, piston-flow microreactor.

Catalytic Hydroprocessing

The acidic fractions were used as 0.25 wt% solutions in cyclohexane, and these feed solutions were saturated with hydrogen at room temperature. CS₂ (0.1 wt%) was added to the feeds to ensure that the catalyst remained in a sulfided state. The reaction conditions were 350°C and 120 atm. Space velocities ranged from 0.05 to 3.2 g of acid fraction/(g of catalyst·h). A more detailed description of the reactor system and its operation has been published (Li et al., 1984B). The samples characterized in this work were the ones described previously by Li et al.

Analysis of the Reactants and Products

The Finnigan GC/MS instrument was equipped with a Model 9600 gas chromatograph. The products were resolved in a J and W fused silica capillary column, 30 m x 0.24 mm, with an SE-54 liquid phase. The injection and transfer line(s) were maintained at 250°C. The column temperature was programmed from 50 to 220°C, with a 2°C/min ramp and a 5-min hold at 220°C. UHP helium carrier gas flowed at a rate of 1.5 cm³/min. The liquid sample volume was typically 1 L, without splitting.

The Finnigan 4510 mass spectrometer, which has a mass range of 33 to 400 with a resolution of about 2000, was operated with an electron energy of 70 eV, an emission current of 0.25 ma, and a multiplier voltage of 1200 V. The preamplifier sensitivity range was 10⁻³ a/V, and the preamplifier filter was set at 1000

amu/s. The scanning was done at 0.95 s/scan with a 0.05-s hold. About 10 mass spectra were obtained per GC peak.

A NOVA 4/INCOS 2000 system was employed for handling and storage of the data. The NBS search library of about 31,000 compounds was used for peak identification. The search routine was done in the "purity" mode, whereby the hierarchy of fit was determined by the number of peaks in the unknown that matched the library spectrum, with intensity ratios considered. This mode is different from the "fit" mode, whereby the match of peaks in the library to those in the unknown (without regard to intensities or extra peaks in the unknown) determines the goodness of fit and different from the "reserve fit" mode, whereby the unknown spectrum is matched to the library spectrum in the same way.

In the analysis of the GC/MS data, a peak assignment was considered to be correct, provided that (1) the number of points characterizing quantitatively the goodness of match between the experimental spectrum and the library spectrum was high, typically 800 or more out of 1000; (2) the next-best fits if they were essentially the same, were isomers of the same compound; and (3) the assignment made good chemical sense. The assignment of an isomer to an empirical formula was considered to be correct if on an overall scale of 1000, the next best fit was 100 less. In some instances, assignments were corroborated by spiking experiments and GC analysis. Often compounds could not be

identified and the best that could be done was the assignment of an empirical formula; for example, it was not possible to determine whether a GC peak represented an isomer of methyltetralin or dimethylindane. These incomplete identifications are still helpful because they allow comparison of the feed and the products in terms of the carbon number and degree of saturation.

Since the data handling package on the GC/MS computer did not provide integrated intensities, it was necessary to match the ion chromatograms with the FID trace from a separate run on the gas chromatograph, which did provide intensity data. n-Dodecane was added to each sample prior to injection at a concentration of 2 wt% as an internal intensity standard. The determination of the concentrations of the individual components was limited in many instances, for one or more of the following reasons: (1) There was no reasonable peak assignment by GC/MS; (2) there was no calculated intensity for a given peak determined by FID/GC as a consequence of the peak's being too small; (3) it was not possible to match the GC/MS peak with a peak on the FID/GC trace because of differences in resolution (e.g., in some cases twin peaks in the FID chromatogram having a single calculated area were resolved into two peaks with different structural assignments in the GC/MS chromatogram). Thus, in some instances, no intensity could be assigned to an identified compound.

RESULTS AND DISCUSSION

Formation of Lower-Molecular-Weight Products

All the products were characterized by GC/MS, and the most detailed analyses were carried out with the two feed samples (the weak- and very-weak-acid fractions) and the products of their conversion at one intermediate space velocity, namely, 0.78 g of acid fraction/g of catalyst·h for the weak-acid fraction and 0.4 g of acid fraction/(g of catalyst·h) for the very-weak-acid fraction. The ion chromatograms of the feeds and products are shown in Figs. 1 and 2. These show that the feeds are devoid of any light materials ($<C_{10}$) and have a narrow range of elution times in the column, which separates the mixture essentially by boiling point. Each feed, especially the weak-acid fraction, is characterized by a relatively small number of major peaks.

The product chromatograms show much wider boiling ranges than those of the feeds. The number of peaks characterizing the products is much greater than the number characterizing the feeds, consistent with the inference that molecules are cracked in the hydroprocessing.

Characterization by Group-Type Analysis

Classification by the degree of saturation. Quantitative data characterizing the molecular-weight-reduction reactions and

others can be obtained from the GC/MS results by consideration of classes (or lumps) of compounds. In the GC/MS analysis, the comparison of an experimental mass spectrum with the library spectra may lead to the recognition of several candidate compounds having the same empirical formula but different structures, each with about the same goodness of fit. Although it may not be possible to assign a structure to a given GC peak, useful conclusions may be inferred as a result of classifying the compound by its degree of unsaturation (or, as will be described later, by other criteria). We divide the compounds into classes defined by the parameter Z , a measure of the degree of (un)saturation; Z is formally defined as the number of hydrogen atoms minus twice the number of carbon atoms in the compound. Typical coal-liquid compounds in classes defined by this criterion are listed in Table I. The Table also lists the $R + DB$ values, which is simply the number of rings and double bonds.

The numbers of compounds identified by GC/MS in each Z class in the feed and product are shown in Figs. 3 and 4. Both feed fractions contain a majority of compounds with values of Z between -6 and -14, with many of the compounds having values of -6, -8, and -14. These correspond to benzenes and phenols ($Z = -6$); tetralins, indanes, and cyclohexylbenzenes and their hydroxy-substituted derivatives ($Z = -8$); and biphenyls and hydroxybiphenyls ($Z = -14$). The products of both fractions have a large number of compounds with $Z = -8$. It is clear that the

dominant products of the hydroprocessing reactions are two-ring compounds, with one ring saturated and the other aromatic.

Products were found in classes not represented significantly in the feeds, namely, the dicycloalkanes ($Z = -2$) and dicycloalkenes ($Z = -4$), which are probably formed by simple hydrogenation of reactant molecules. The possibility of reaction of compounds of the acid fractions with the solvent cyclohexane cannot be ruled out; however, the compounds with $Z = -2$ and $Z = -4$ have at least eight carbons and cannot be accounted for by simple dehydrogenation of cyclohexane.

Product distributions determined from the classification are shown in Figs. 5 and 6 for the weak- and very-weak-acid fractions, respectively. The data are shown as histograms of the area percentages determined from a FID chromatogram for the Z groups of the feeds and products (Refer to Figures 3 and 4 for histograms of the number of compounds in the 2 classes). The areas have been corrected for components added to check some peak assignments, but otherwise they are not normalized. The area of the chromatogram assigned to Z classes is less than the total area of the chromatogram, since not all ion chromatogram peaks from the GC/MS experiment were assignable to any empirical formula, and not all of the peaks in the FID chromatogram had calculated areas. Further, the degree of match between the FID and ion chromatograms limited the number of areas that could be

assigned to Z classes. For these reasons, the compounds which were eluted at the high-molecular-weight end of each chromatogram are underrepresented in Figs. 5 and 6.

In Fig. 5 (the histogram for the very-weak-acid fraction) 76% of the product and about 40% of the feed was assigned to Z classes. Although the relative amounts of material from the feed and product in certain Z classes are determined only qualitatively as a consequence of the differing degrees of successful peak assignment, it is clear that there was a decrease in the amount of material which falls in classes $Z = -6$ and $Z = -14$ as a result of the hydrotreatment of the very-weak-acid fraction; there are fewer benzenes (or phenols) and biphenyls in the product than in the feed. A marked loss of compounds in the class $Z = -14$ also occurred as a result of the hydrotreatment of the weak-acid fraction, as shown in Fig. 6. There was a significant increase in the number of compounds in the class $Z = -8$.

Several reactions could account for these changes. Biphenyls (or hydroxybiphenyls) undergoing hydrogenation of one ring to give cyclohexylbenzenes could account for the decrease in the class $Z = -14$ and the increase in the class $Z = -8$. Hydrogenation of naphthalenes ($Z = -12$) to give tetralins or indanes is another possibility, but the very small amount of feed material in the class $Z = -12$ makes it seem highly unlikely. The

hydrogenation of biphenyls, cyclohexylbenzenes, and tetralins may be responsible for the formation of products in the classes $Z = -2$ and $Z = -4$.

A more comprehensive picture of the reaction patterns emerges from consideration of the (less complete) data obtained over the full range of space velocities. Fig. 7 is a plot of the concentrations of the lumps defined by the Z number in the weak-acid fraction as a function of inverse space velocity. Although there is considerable scatter in the data (indicative of the varying degrees of success in the matching of GC/MS to FID GC data), there is a clear trend of decreasing concentration in the classes $Z = -14$ (e.g., biphenyl) and increasing concentration in $Z = -8$ (e.g., tetralin, indane, and cyclohexylbenzene). There was only a low concentration of the class $Z = -6$ (e.g., phenol, benzenes) in the feed, and even lower concentrations were observed in the products.

Not shown in this figure are the increases in the classes $Z = -2$ and $Z = -4$. These are possibly two- or three-ring saturated structures or cycloalkenes. The concentrations of these lumps increase from zero in the feed to about 3% in the most severely hydrotreated product. Some compounds initially present in the groups $Z = -8$ and $Z = -14$ may have been converted into these totally or almost totally hydrogenated products.

The product distributions found with the weak-acid fraction are consistent with the known reaction networks for naphthalene, benzene, and biphenyl obtained with the pure compounds under comparable conditions (Sapre and Gates, 1981). At a space velocity for which the lump with $Z = -14$ (consisting of biphenyls and hydroxybiphenyls) is about one-third converted, only a small concentration of saturated compounds typified by bicyclohexyl ($Z = -2$) is expected. The relative concentrations of products in the classes $Z = -6$, -8 , and -14 are plotted as a function of inverse space velocity in Fig. 7. The trend is a reduction in concentration of the group $Z = -14$ (e.g., biphenyl) and an increase in concentration of the group $Z = -8$ (e.g., cyclohexylbenzene) with increasing severity of hydrotreatment.

Classification by Carbon Number Distribution. Further information about the molecular-weight-reducing reactions is provided by histograms of the carbon number distributions (Figs. 8 and 9). Fig. 8, which shows the composition of the very-weak-acid feed and the product obtained at an intermediate space velocity, can be interpreted only qualitatively, since unequal parts of the feed and product were identified; only a small part of the very-weak-acid fraction was identified. We infer that cracking occurred, since eight- and nine-carbon compounds were found in the product but not in the feed. The data for the weak-acid fraction (Fig. 9) provide more evidence of cracking; the concentrations of 12-, and 13-carbon molecules

decreased substantially, and the concentrations of nine- and ten-carbon compounds increased.

Cracking accompanying hydrogenation in the presence of sulfided Co-Mo/Al₂O₃ and related catalysts, particularly removal of methyl groups from aromatic rings, is well known (Patzner et al., 1979). We infer that the severe reduction in the 11- and 13-carbon species, which include methyl-substituted hydroxytetralin, hydroxybiphenyl, and cyclohexylphenol, is in part a result of scission of methyl groups from the rings. Specifically, the nine-carbon species in the product might have been formed by cracking of methyl groups from dimethylhydroxyindane or from the methylindane rearrangement product formed from tetralin. The apparent increase in the concentration of 14-carbon species may be an indication of cracking of compounds too large to be identified from the GC/MS data.

Classification by functional groups. The patterns of change in the degree of unsaturation and carbon number distribution provide a partial picture of the chemical changes occurring upon hydrotreatment; further information can be derived by consideration of lumps defined according to functional groups. Table II is a summary giving the number of compounds in a particular class for the very-weak-acid fraction and the product of its hydroprocessing analyzed in greatest detail--that obtained

at a space velocity of 0.4 g of acid fraction/(g of catalyst·h). The data show that carbonyl compounds, one-ring phenols, and two-ring phenols appear to have reacted completely at the intermediate space velocity. Other organo-oxygen compounds, such as those incorporating phenoxy, methoxy, or furan groups, were found in the product and are inferred to be less reactive. (The data referred to here do not determine whether these groups were reduced in concentration; we return to this question in considering the pure-compound data.) Most of the organonitrogen compounds were converted; compound types observed in the product but not in the feed include cyclo- and dicycloalkanes, two-ring aromatics, and a large number of fused cycloalkylaromatics, such as tetralins and indanes. Four two-ring phenols were found in the feed and four cycloalkyl compounds in the product, along with a number of two-ring aromatics (naphthalenes and biphenyls). It is likely that the hydroxybiphenyls and cyclohexylphenols (two-ring phenols) were converted into these derivatives of biphenyl and cyclohexylbenzene.

The data of Table III, for the weak-acid fraction, show similar patterns. Organonitrogen and carbonyl compounds reacted completely, and two-ring phenols were reduced in number, although they were not all removed. This last observation does not imply that these phenols are substantially different from those in the very-weak-acid fraction, since the latter fraction (Table III) was more severely treated, having been converted at half the

weight hourly space velocity of the former (Table II). The products of the reaction not present in the feed are similar to those found in the products of the very-weak-acid fraction. The predominant products are fused cycloalkylaromatics of the tetralin or indane family, cyclo- and dicycloalkanes, two- and three-ring aromatics, and cycloalkylbenzenes.

Summary. Examination of the feed and products in terms of the lumps leads to the following conclusions: (1) The feeds contain a relatively small number of major components which, upon hydroprocessing, are reduced in concentration, forming many more product molecules. (2) In addition to the removal of the typical oxygen functionality, the hydroxyl group, there was significant ring hydrogenation. (3) There is evidence of cracking, both from the formation of compounds having fewer carbons than the feed compounds and from shifts in carbon number distributions among the compounds existing in the feeds; this cracking is inferred to involve principally the methyl substituents bonded to rings.

Conversions of Individual Compounds

A number of individual compounds in the feeds and products have been identified with a high degree of confidence. These are listed for the weak acids in Table IV with their GC retention times. Far fewer compounds were identified in the very-weak-acid fraction, and these are not included. The individual-compound data provide the opportunity for

determination of quantitative reactivities.

Formation of nine-carbon products from the weak-acid fraction is shown as a function of inverse space velocity in Fig. 10. The concentrations shown in the plots are relative to that of the internal standard, *n*-dodecane, which was added to the products at a concentration of 2 wt%. The C_9H_{10} aromatic species is formed faster than the C_9H_{16} dicycloalkane (or cycloalkene). All the curves appear to pass through the origin, which implies that the products are primary, i.e., formed directly from compounds present in the feed. The concentrations of both the aromatic and dicycloalkene pass through maxima; the shapes of the curves suggest that these products undergo conversion in secondary reactions.

Formation of the ten-carbon products from the weak-acid fraction is shown in Fig. 11. Each of the four products has the composition $C_{10}H_{12}$. These results indicate some different types of reactions. Three of the curves pass through the origin; we infer that these three products (tetralin, an unsaturated C_4 -substituted benzene, and either a substituted benzene or indane) are formed directly from reactant molecules. This inference is not surprising in light of the fact that hydroxytetralin (tetrahydronaphthol) is a major feed component (Li *et al.*, 1984B).

The other $C_{10}H_{12}$ isomer, which is either a methylindane or an unsaturated alkylbenzene, is formed at a higher rate, but only after some induction period, implying that this is a secondary product. Since only one five-membered ring compound was identified in the feed, we infer that some indanes may have been formed as secondary products while others were formed directly. The isomerization of tetralin to give methylindane and substituted benzenes is well known, occurring via free radical intermediates (McNeil *et al.*, 1983) or in the presence of typical hydrotreating catalysts (Ruberto, 1980).

Although most of the curves in Fig. 11 level off at the highest value of inverse space velocity, the tetralin concentration passes through a maximum; this result is consistent with the suggestion that tetralin is first produced by hydrodeoxygenation of hydroxytetralin, which subsequently isomerizes to give methylindane. Methylindane could also crack to give indane.

A similar plot for the eleven-carbon products formed from the weak-acid fraction is shown in Fig. 12. These products are identified as an oxygenated species, $C_{11}H_{14}O$ (which appears to be a primary product undergoing subsequent conversion) and three isomers of $C_{11}H_{14}$. The $C_{11}H_{14}$ structures may be substituted benzenes, tetralins, and/or indanes; they all appear to be secondary products.

The data for the twelve-carbon products formed from the weak-acid fraction are shown in Fig. 13. The primary product, $C_{12}H_{22}$, is probably a saturated two-ring compound such as bicyclohexyl or possibly a substituted cycloalkene. A similar type of compound, C_9H_{16} , was formed at an almost identical rate. $C_{12}H_{16}$, which is a C_2 alkyltetralin or possibly an unsaturated alkylbenzene, is formed at a higher rate; its concentration levels off at the highest inverse space velocity. A much higher rate of formation was found for cyclohexylbenzene, $C_{12}H_{16}$, although it may be a secondary product. Cyclohexylbenzene is expected to be the primary hydrodeoxygenation product of cyclohexylphenol and a product of the hydrogenation and hydrodeoxygenation of phenylphenol.

The formation of methylcyclohexylbenzene is shown in Fig. 14. This primary product is formed at a rate similar to that observed for cyclohexylbenzene. The formation of another C_{15} product, methylbiphenyl, is also shown in Fig. 14; this is also a primary product, perhaps of hydroxymethylbiphenyl.

The reactivities of organo-oxygen compounds in the weak-acid fraction are shown in Fig. 15. Straight-line plots on this figure indicate first-order reaction; the data are fairly well represented by this form of kinetics, but there is wide scatter. The most reactive of these compounds is

cyclohexylphenol, followed by three fused hydroxy-cycloalkylbenzenes, hydroxytetralin or tetrahydronaphthol, methyltetrahydronaphthol, and dimethylhydroxyindane. Still less reactive compounds include methylphenylphenol, phenylphenol, and a compound identified only as $C_{13}H_{12}O$, which is known to contain two aromatic rings; it may be either a methylphenoxybenzene or a methylphenylphenol. It is not known if the initial rise in concentration of cyclohexylphenol is real, however, it is reported to be an intermediate in the HDO network of phenylphenol (Krishnamurthy *et al.*, 1981). The rate constants of these compounds are summarized in Table V. The rate constants were calculated from the inverse space velocity (g catalyst-hr/g feed) needed to reduce the concentration of a species to half its initial value, the concentration of the acid in the feed solution (0.0025 g acid/g solution); a density factor of 411 g/l of solution at the reaction condition, and the natural log of 0.5. The values are in satisfactory agreement with those of Li *et al.* (1984B); however, there are inconsistencies in the data, depending on whether the conversions were determined from absolute GC peak areas or ratios of those areas to the area of the *n*-dodecane standard. The data determined with reference to *n*-dodecane are believed to be the more reliable.

These reactivity data show that the methyl-substituted compounds react somewhat faster than the unsubstituted species of

the same type. But since the data provide a comparison of the rates of disappearance of the reactants and not of hydrodeoxygenation, we emphasize that there are several pathways for conversion of the reactants besides hydrodeoxygenation, including scission of a methyl group, isomerization, and ring hydrogenation. In the catalytic hydrogenation of 1-methylnaphthalene, the loss of a methyl group has been found to be faster than hydrogenation of an aromatic ring (Patzner et al., 1981).

Comparison with Reaction Networks Determined with Pure Compounds

Identification of the compounds in the weak-acid feed and the hydroprocessing products shows that most of the observations are qualitatively consistent with the literature for catalytic hydrodeoxygenation of pure compounds. Kinetics and hydroprocessing reaction networks have been reported for 1-naphthol (Li et al., 1984A), dibenzofuran, o-phenylphenol, and o-cyclohexylphenol (Krishnamurthy et al., 1981). Tetrahydronaphthol, one of the major components in the feed, is expected to be converted mostly into tetralin (tetrahydronaphthalene), which is then converted predominantly into the trans-decalin (decahydronaphthalene) and smaller amounts of naphthalene and cis-decalin (Li et al., 1984A). Tetralin is the only compound identified in the products of hydrodeoxygenation that is likely to be derived from

tetrahydronaphthol. As can be seen in Fig. 11, tetralin appears to be a primary product which reacts to form additional compounds. Compounds such as decalin, naphthalene, or the isomerization product, methylindane, may be produced, but at concentrations too low for detection in these experiments.

Cyclohexylphenol and phenylphenol were both identified in the feed, and some of the reported hydrodeoxygenation products of these compounds (Krishnamurthy et al., 1981) have been identified: Bicyclohexyl and cyclohexylbenzene were found in the products, but biphenyl, phenol, cyclohexane, and phenyl hexanol were not. Phenol, which reacts rapidly to give unidentified products (probably two-carbon or smaller) and cyclohexane, which was used as the solvent in this reaction system, could not be detected with our methods. Cyclohexylbenzene was found to be the predominant 12-carbon product (Fig. 13), probably a secondary product. Bicyclohexyl, a primary product, was found in much lower concentration. Cyclohexylbenzene is a major product of the hydrodeoxygenation of phenylphenol; since the rate constant reported by Krishnamurthy et al. (1981) for the conversion of biphenyl into cyclobexylbenzene is nearly twice that for the formation of biphenyl from phenylphenol, biphenyl would be expected to be formed in low concentration, which may explain why it was not detected in the products.

Phenylhexanol is another product of the

hydrodeoxygenation of phenylphenol that was not detected. However, this compound reacts further to give unspecified hydrocarbon products at unknown rates. The products of this and other compounds which to go "hydrocarbons" may constitute some of the new, lighter products (C₉ and C₁₀ hydrocarbons) found in the weak acid hydrotreating products.

Summary

As a result of hydroprocessing of the acidic fractions of the coal liquid, there is a broadening of the range of molecular weights, reflecting the formation of lighter components. The distribution of carbon numbers of the products confirms this change. In addition to hydrodeoxygenation and hydrocracking, hydrogenation of the feed species also occurs, particularly in the biphenyl class of compounds, which decrease in concentration with increased hydrotreating severity, as compounds of the tetralin, indane, and cyclohexylbenzene class are formed.

Many compounds of the naphthol and phenylphenol type were identified in the feeds and generally appear to react by the reaction pathways determined in pure-compound experiments. Reactivities of the compounds identified in terms of disappearance are in the order: cyclohexylphenol > dimethylhydroxyindane $\approx$ methyltetrahydronaphthol $\approx$ tetrahydronaphthol > methylphenylphenol phenylphenol. Methyl substitution of an organooxygen compound increases probably

mostly as a result of providing an additional pathway for reaction (hydrodealkylation). Neither this observation nor the above order of reactivity implies anything about the ease of oxygen removal.

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FIGURE CAPTIONS

- Fig. 1A. Ion chromatogram of the very-weak-acid feed.
- Fig. 1B. Ion chromatogram of the very-weak-acid product obtained at a space velocity of 0.4 g of acid fraction/(g of catalyst h).
- Fig. 2A. Ion chromatogram of the weak-acid feed.
- Fig. 2B. Ion chromatogram of the weak-acid product obtained at a space velocity of 0.78 g of acid fraction/(g of catalyst h).
- Fig. 3. Number of compounds identified by Z-number in the very-weak-acid fraction and in the product obtained at a space velocity of 0.4 g of acid fraction/(g of catalyst h).
- Fig. 4. Number of compounds identified by Z-number in the weak-acid fraction and the product obtained at a space velocity of 0.78 g of acid fraction/(g of catalyst h).
- Fig. 5. Relative amounts of compounds by Z-number in very-weak-acid fraction and product obtained at a space velocity of 0.4 g of acid fraction/(g of catalyst h).
- Fig. 6. Relative amounts of compounds by Z-number in weak-acid fraction and product obtained at a space velocity of 0.78 g of acid fraction/(g of catalyst h).
- Fig. 7. Conversion of compounds in the weak-acid fraction at 350°C and 120 atm; reactants are classified by Z-number groups.
- Fig. 8. Relative amounts of compounds by carbon number in the very-weak-acid fraction and in the product obtained at a space velocity of 0.4 g of acid fraction/(g of catalyst h).
- Fig. 9. Relative amounts of compounds by carbon number in the weak-acid fraction and in the product obtained at a space velocity of 0.78 g of acid fraction/(g of catalyst h).
- Fig. 10. Formation of C₉ products from the weak-acid fraction at 350°C and 120 atm.
- Fig. 11. Formation of C₁₀ products from the weak-acid fraction at 350°C and 120 atm.

Fig. 12. Formation of C_{11} products from the weak-acid fraction at 350°C and 120 atm.

Fig. 13. Formation of C_{12} products from the weak-acid fraction at 350°C and 120 atm.

Fig. 14. Formation of C_{13} products from the weak-acid fraction at 350°C and 120 atm.

Fig. 15. First-order kinetics plot for conversion of individual organooxygen compounds in the weak-acid fraction at 350°C and 120 atm.

Z Classes of Typical Molecular
Structures in Coal Liquids

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R+DB	Z CLASS	HYDROCARBON	NITROGEN*	OXYGEN	SULFUR
0	+2	PARAFFIN (R)	R-NH ₂ ALIPHATIC AMINE	R-OH ALIPHATIC ALCOHOL R-O-R ALIPHATIC ETHER	R-SH ALIPHATIC THIOL R-S-R ALIPHATIC SULFIDE
1	0	OLEFIN R-R CYCLOPARAFFIN	-R ALKYLCYCLOC PYRROLIDINE	R-CHO ALDEHYDE R-CR KETONE	THIANE
2	-2	DICYCLOPARAFFIN	DIHYDROPYRROLIDINE DECAHYDROQUINOLINE	DIHYDROFURAN CYCLIC - KETONES	THIADECAHYDRO- NAPHTHALENE
3	-4	CYCLOHEXADIENE	PYRROLE	FURAN	THIOPHENE
4	-6	BENZENE	PYRIDINE	PHENOL	BENZETHIOL
5	-8	TETRALIN INDANE	DIHYDROINDOLE	INDANOL	THIATETRALIN
6	-10	INDENE	INDOLES	INDENOL	BENZOTHIOPHENE
7	-12	NAPHTHALENE	QUINOLINE	NAPHTHOL	NAPHTHOBENZO- THIOPHENE
8	-14	ACENAPHTHENE BIPHENYL	DIPHENYLAMINE	PHENYLPHENOL	NAPHTHEMENBENZO- THIOPHENE
9	-16	FLUORENE	CARBAZOLE	DIBENZOFURAN	DIBENZOTHIOPHENE
10	-18	ANTHRACENE	ACRIDINE	ANTHRONE	THIAANTHRACENE
11	-20	PHENYL NAPHTHALENE	DIHYDROBENZO CARBAZOLE	NAPHTHOBENZO- DIHYDROFURAN	DIPHENYLTHIOPHENE
12	-22	PYRENE		OXADIHYDROPYRENE	PHENYL TETRALIN- THIOPHENE
13	-24	BENZANTHRACENE	NAPHTHOQUINOLINE	BENZANTHRONE	NAPHTHYLBENZO- THIOPHENE
14	-26	DINAPHTHYL	DINAPHTHYLAMINE	DINAPHTHYLKETONE	PHENYL NAPHTHYL- THIOPHENE
15	-28	BENZOPYRENE

* Z Class should be increased by [+1] to account for the nitrogen valence

TABLE II

Number of Compounds by Type in the Very Weak Acid
Feed and Hydrotreated Product

<u>Compound Type</u>	<u>Feed</u>	<u>Product^a</u>
Benzene	9	13
1-Ring Phenols	2	NF ^b
2-Ring Phenols	4	NF
Carbonyl Compounds ^c	8	NF
Ethers ^d	6	6
Nitrogen Compounds	6	1
3-Ring Aromatics	1	2
Cyclic Alkanes, Alkenes	NF	7
2-Ring Aromatics	NF	5
Fused cycloalkyl Aromatics ^e	NF	15
Cycloalkyl Aromatics	NF	4

^aObtained at a space velocity of 0.4 g of fraction/
(g of catalyst·h).

^bNot found.

^cFuranone is considered to be a carbonyl compound.

^dEthers include methoxy, phenoxy, and furan.

^eFused cycloalkyl aromatics include tetralin and indanes.

TABLE III
Number of Compounds by Type in the Weak Acid Feed
and Hydrotreated Product

<u>Compound Type</u>	<u>Feed</u>	<u>Product^a</u>
Benzenes	4	3
2-Ring Phenols	8	3
Carbonyl Compounds	1	NF ^b
Ethers	2	3
Nitrogen Compounds	2	NF
Cyclo- and dicycloalkanes, alkenes	NF	9
Fused cycloalkylaromatics	NF	14
Two-Ring Aromatics or ???	NF	5
Three-Ring Aromatics	NF	3
Cycloalkylbenzenes	NF	3

^aObtained at a space velocity of 0.78 g of fraction/
(g of catalyst·h).

^bNot found.

TABLE IV

Weak Acid Feed GC/MS Peak Assignments

<u>Retention Time, s</u>	<u>Z Number</u>	<u>Empirical Formula</u>	<u>Assignment</u>
2657	- 8	C ₁₀ H ₁₂ O	C ₄ phenol?
2674	- 6	C ₁₂ H ₁₈	C ₆ alkylbenzene
2721	- 6	C ₁₂ H ₁₈	C ₆ alkylbenzene
2753	- 8	C ₁₀ H ₁₂ O	Tetrahydronaphthol
2774	- 6	C ₁₂ H ₁₈	C ₆ alkylbenzene
2805		O Compound?	C ₅ phenol?
2843	- 8	C ₁₀ H ₁₂ O	Tetrahydronaphthol
2888	- 6	C ₁₂ H ₁₈	C ₆ alkylbenzene
2923	- 8	C ₁₁ H ₁₄ O	?
2933	- 6	C ₁₂ H ₁₈	C ₆ alkylbenzene
2964	-14	C ₁₂ H ₁₀ O	Phenylphenol
3063	-14	C ₁₂ H ₁₀ O ₂	Dimethylbenzofuranone
3092	- 8	C ₁₁ H ₁₄ O	Methyltetrahydronaphthol
3170	- 8	C ₁₂ H ₁₆ O	Cyclohexylphenol
3216	- 6	C ₁₃ H ₂₀	C ₇ alkylbenzene
3305	-14	C ₁₃ H ₁₂ O	Methylphenylphenol
3437	- 8	C ₁₂ H ₁₆ O	Cyclohexylphenol
3742	- 8	C ₁₃ H ₁₈ O	Methylcyclohexylphenol or methoxycyclohexyl benzene
3757	-14	C ₁₃ H ₁₂ O	Phenoxy, methoxy, or phenol
4052	-14	C ₁₃ H ₁₂ O	Phenoxy or phenol
4082	-14	C ₁₃ H ₁₂ O	Phenoxy or phenol
4367	-14	C ₁₄ H ₁₄ O	C ₂ phenoxybenzene
4404		C ₁₃ or C ₁₄	O compound
4442		?	A benzene dicarboxylic acid ester
4561		C ₁₅ H ₁₂ N ₂ ?	Diphenyl N compound
4624		O Compound	2 to 5 O atoms
4943		C ₁₅ H ₁₂ N ₂ ?	Diphenyl N compound

Weak Acid Product GC/MS Peak Assignments

684	- 6	C ₉ H ₁₂	C ₃ benzene
761	- 2	C ₉ H ₁₆	Cycloalkene
844	- 4	C ₉ H ₁₄	Spiroononene
928	- 8	C ₉ H ₁₀	Unsat. C ₃ benzene
977	- 4	C ₁₀ H ₁₆	Cycloalkene
990	- 4	C ₁₀ H ₁₆	C ₄ cyclohexene
1002	- 4	C ₁₀ H ₁₆	Unsat. cyclic hydrocarbon
1037	- 4	C ₁₀ H ₁₆	Unsat. cyclic hydrocarbon
1050	- 4	C ₁₀ H ₁₆	Unsat. cyclic hydrocarbon

1061	- 4	C ₁₀ H ₁₆	Unsat. cyclic hydrocarbon
1098	- 8	C ₁₀ H ₁₂	Unsat. C ₄ benzene
1119	- 8	C ₁₀ H ₁₂	Unsat. C ₄ benzene
1281	- 8	C ₁₁ H ₁₄	Unsat. C ₄ benzene
1297	- 8	C ₇ H ₈ O	Methylphenol
1328	- 8	C ₁₀ H ₁₂	Indene or unsat. benzene
1348	- 8	C ₁₁ H ₁₄	Indene or unsat. benzene
1373	- 8	C ₁₀ H ₁₂	Indene or unsat. benzene
1418	- 8	C ₁₀ H ₁₂	Tetralin
1472	- 4	C ₁₁ H ₁₈	Cycloalkene
1512	-12	C ₁₀ H ₈	Naphthalene or azulene
1527	- 8	C ₁₁ H ₁₄	Dihydrodimethylindene
1535	- 8	C ₁₁ H ₁₄	Dihydrodimethylindene
1550	- 8	C ₁₁ H ₁₄	C ₅ benzene or C ₂ indene
1570	- 8	C ₁₁ H ₁₄	Dimethyldihydroindene
1641	- 8	C ₁₁ H ₁₄	Methyltetralin
1677	- 8	C ₁₁ H ₁₄	C ₅ benzene or methyltetralin
1722	- 8	C ₁₁ H ₁₄	C ₅ benzene or methyltetralin
1746	- 2	C ₁₂ H ₂₂	Bibyclo alkane or cycloalkene
1836	- 8	C ₁₁ H ₁₄	Dimethyldihydroindene
1840	- 8	C ₁₁ H ₁₄	Methyltetralin
1910	- 8	C ₁₂ H ₁₆	C ₂ tetralin or C ₆ benzene
1952	- 8	C ₁₁ H ₁₄ O?	
1969	-12	C ₁₁ H ₁₀	Methylnaphthalene
2035	-12	C ₁₁ H ₁₀	Methylnaphthalene
2064	- 8	C ₁₂ H ₁₆	Cyclohexylbenzene
2086	- 8	C ₁₂ H ₁₆	C ₂ tetralin or C ₆ benzene
2120	- 8	C ₁₂ H ₁₆	C ₂ tetralin or C ₆ benzene
2283	- 8	C ₁₃ H ₁₈	C ₇ benzene
2297	- 8	C ₁₃ H ₁₈	C ₇ benzene
2315	-14	C ₁₂ H ₁₀	Biphenyl?
2373	- 8	C ₁₃ H ₁₈	C ₇ benzene
2394	-14	C ₁₃ H ₁₂	C ₁ diaromatic
2408	- 8	C ₁₃ H ₁₈	Methylcyclohexylbenzene
2480	-10	C ₁₂ H ₁₄	Monoaromatic
2567	- 6	C ₁₁ H ₁₆	C ₅ benzene
2703	- 6	C ₁₂ H ₁₈	Diethylxylene
2728	-14	C ₁₃ H ₁₂	Methylbiphenyl
2751	- 8	C ₁₁ H ₁₄	Methyltetralin
2792	- 8	C ₁₂ H ₁₆	Dimethyltetralin
2858	- 8	C ₁₂ H ₁₆	Dimethyltetralin
2866	- 6	C ₁₂ H ₁₈	C ₆ benzene
2908	-14	C ₁₂ H ₁₀	Hydroxybiphenyl
3011	- 6	C ₁₂ H ₁₈	C ₆ benzene
3064	-14	C ₁₄ H ₁₄	C ₂ biphenyl
3082	-16	C ₁₃ H ₁₀	Fluorene or phenalene
3120	-14	C ₁₄ H ₁₄	2 Rings 2 methyl groups
3156	-16	C ₁₄ H ₁₂	Methylfluorene?
3243	-14	C ₁₃ H ₁₂ O	Methoxybiphenyl
3286	-14	C ₁₃ H ₁₂ O?	Methoxybiphenyl?
3434	-14	C ₁₅ H ₁₆	Phenylmethylxylene

3477	-10	C ₁₅ H ₂₀	Bicyclo C ₉ benzene
3486	-16	C ₁₄ H ₁₂	Methylfluorene
3494	-16	C ₁₄ H ₁₂	Methylfluorene
3518	-16	C ₁₄ H ₁₂	Methylfluorene
3620	-14	C ₁₄ H ₁₄ O?	
3658	-14	C ₁₄ H ₁₄ O ₂ ??	
3680	-14	C ₁₃ H ₁₂ O	Phenol, methoxy, or phenoxy
3813	-18	C ₁₅ H ₁₂	Dibenzocycloheptene
3830	-18	C ₁₅ H ₁₂	Dibenzocycloheptene
3882	-16	C ₁₅ H ₁₄	2 Rings 3 alkyl carbons
3978	-14	C ₁₃ H ₁₂ O	Phenoxy or phenol
4284	-14	C ₁₄ H ₁₄ O	Methyl, methyl phenoxy benzene

TABLE V

Rate Constants for Disappearance of Organooxygen Compounds

<u>Formula</u>	<u>Z Number</u>	<u>Name</u>	<u>Temp., °C</u>	<u>Rate Constant, (this work)</u>	<u>L/(g of catalyst·s) (Li et al., 1984B)</u>
$C_{12}H_{16}O$	- 8	cyclohexylphenol	350	6.2×10^{-4}	4.5×10^{-4}
$C_{11}H_{14}O$	- 8	dimethyldihydroxyindane	350	4.6×10^{-4} $(2.3 \times 10^{-4})_a$	
$C_{11}H_{14}O$	- 8	methyltetrahydronaphthol	350	4.5×10^{-4}	
$C_{10}H_{12}O$	- 8	tetrahydronaphthol	350	4.2×10^{-4} $(2.5 \times 10^{-4})_a$	1.9×10^{-4}
$C_{13}H_{12}O$	-14	methylphenylphenol	350	2.0×10^{-4}	1.5×10^{-4}
$C_{12}H_{10}O$	-14	phenylphenol	350	1.8×10^{-4} $(7.3 \times 10^{-5})_a$	8.3×10^{-5}
$C_{13}H_{12}O$	-14	methylphenylphenol or methylphenoxybenzene	350	1.4×10^{-4}	
$C_{10}H_8O$	-12	1-naphthol	200	3.8×10^{-5}	

aDetermined on the basis of a comparison with the n-dodecane spike, with the datum at 3.22 g of acid fraction/(g of catalyst·h) ignored.

FIGURE 1A

FIGURE 1B

FIGURE 2A

FIGURE 2B

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE 13.

FIGURE 14

FIGURE 15

VI. Publications Resulting from this DOE Project

1. "Hydrodesulfurization of Benzo[b]naphthol[2,3-d]thiophene Catalyzed by Sulfided CoO-MoO₃/γ-Al₂O₃: The Reaction Network," A. V. Sapre, D. R. Broderick, D. Fraenkel, B. C. Gates, and N. K. Nag, AIChE Journal **26**, 690 (1980).
2. "Hydrogenation of Aromatic Hydrocarbons Catalyzed by Sulfided CoO-MoO₃/γ-Al₂O₃: Reactivities and Reaction Networks," A. V. Sapre and B. C. Gates, Ind. Eng. Chem. Proc. Des. Dev. **20**, 68 (1981).
3. "Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalyzed by Sulfided CoO-MoO₃/γ-Al₂O₃: The Reaction Kinetics," D. H. Broderick and B. C. Gates, AIChE Journal **27**, 663 (1981).
4. "Catalytic Upgrading of Coal Liquids: Preparation and Characterization of Microreactor Feeds," L. Petrakis, R. G. Ruberto, D. C. Young, S. Katti, D. W. B. Westerman, and B. C. Gates, Proceedings, International Conference on Coal Science, Düsseldorf, p. 516 (1981).
5. "Hydrogenation of Biphenyl Catalyzed by Sulfided CoO-MoO₃/γ-Al₂O₃: The Reaction Kinetics," A. V. Sapre and B. C. Gates, Ind. Eng. Chem. Proc. Des. Dev. **21**, 86 (1982).
6. "Hydrogenation of Aromatic Compounds Catalyzed by Sulfided CoO-MoO₃/γ-Al₂O₃," D. H. Broderick, A. V. Sapre, B. C. Gates, H. Kwart, and G. C. A. Schuit, J. Catal. **73**, 45 (1982).
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10. "Hydrodeoxygenation of 1-Naphthol: Activities and Stabilities of Molybdena and Related Catalysts," M. W. Vogelzang, C.-L. Li, G. C. A. Schuit, B. C. Gates, and L. Petrakis, J. Catal., **62**, 1375 (1983).
11. "Capillary Column Gas Chromatography with Sulfur- and Nitrogen-Specific Hall Detectors for Determination of Kinetics of Hydroprocessing Reactions of Individual Compounds in Coal-Liquid Fractions," D. W. B. Westerman, S. S. Katti, M. W. Vogelzang, C.-L. Li, B. C. Gates, and L. Petrakis, Fuel, **62**, 1376 (1983).
12. "Functional Group Analysis of Synthetic Fuels," D. Allen, L. Petrakis, G. R. Gavalas, and B. C. Gates, Anal. Chem., **54**, 1557 (1983).

13. "Hydroprocessing of Organo-Oxygen Compounds in Coal Liquids Catalyzed by Sulfided Ni-Mo/ γ -Al₂O₃," C.-L. Li, S. S. Katti, B. C. Gates, and L. Petrakis, J. Catal., XX, XXX (1984).
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VII. Personnel/Acknowledgments

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This work is also the subject of a paper to be published:

"Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions. 5. Conversion of the Acidic Fractions Characterized by Gas Chromatography/Mass Spectrometry," by D. W. Grandy,*L. Petrakis,* C.-L. Li, and B. C. Gates.

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Personnel at the University of Delaware in addition to Li and Gates include S. S. Starry and S. K. Banerjee.